



Thermal and oxidation stability of organo-fluorine compound-mixed electrolyte solutions for lithium ion batteries



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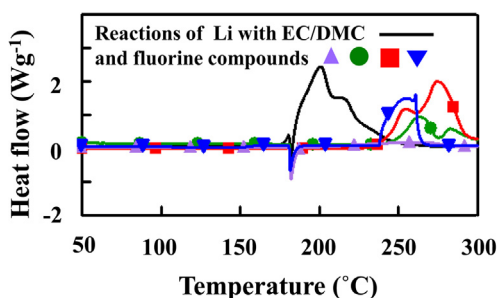
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HIGHLIGHTS

- Organo-fluorine compounds have much lower reactivity with Li than EC/DMC.
- Organo-fluorine compounds improve thermal stability of electrolyte solution.
- Fluorine compounds improve electrochemical oxidation stability of electrolyte solution.
- Organo-fluorine compounds increase first coulombic efficiencies in PC-containing solution.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermal and oxidation stability of fluorine compound-mixed electrolyte solutions have been investigated. Charge/discharge behavior of natural graphite electrode has been also examined in the same electrolyte solutions. Fluorine compounds demonstrate much lower reactivity with metallic Li than ethylene carbonate/dimethyl carbonate. Fluorine compound-mixed electrolyte solutions show the lower reactivity with LiC_6 and the smaller exothermic peaks due to decomposition of electrolyte solutions and surface films than original solutions without fluorine compound. Oxidation currents are also smaller in fluorine compound-mixed electrolyte solutions than in original ones. First coulombic efficiencies in fluorine compound-mixed electrolyte solutions are similar to those in original ethylene carbonate-based solutions except one case. Mixing of fluorine compounds highly increase first coulombic efficiencies of natural graphite electrode in propylene carbonate-containing solution.

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1. Introduction

Lithium ion batteries with high rate charge and discharge are urgently requested for their application to hybrid cars and electric vehicles. However, lithium ion batteries have a possibility of firing and/or explosion at high temperatures, by short circuit formation,

by overcharging and so on since they use flammable organic solvents. The high safety is now one of the most important issues for the practical use of lithium ion batteries. High oxidation stability of organic solvents is particularly needed for the use of 5 V class cathodes. Several different type compounds have been examined to improve the oxidation stability of electrolyte solutions. Phosphorus compounds such as phosphates usually show good flame retardant properties [1–31]. Mixing of ionic liquids is also useful to increase the oxidation stability of electrolyte solutions [32–36]. In addition to these compounds, organo-fluorine compounds are new

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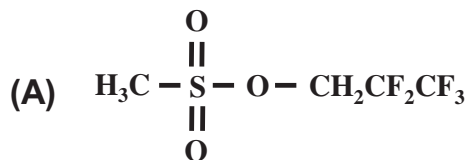
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candidates to improve thermal and oxidation stability of electrolyte solutions [37–47]. Fluorine substitution of organic compounds normally increases the stability against oxidation [41,42]. Partially fluorinated carbonates, ethers and esters have been studied because they are miscible with solvent mixtures consisting of cyclic and linear carbonates such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC) [41–44]. Miscibility of highly fluorinated organic compounds with EC and PC having high dielectric constants is low. Furthermore highly fluorinated organic compounds reduce the solubility of inorganic electrolyte such as LiPF_6 . Therefore partially fluorinated carbonates, ethers and esters are preferable as new solvents with high oxidation stability. It was recently shown that fluorine-containing carbonates, ethers and esters improve thermal and oxidation stability of electrolyte solutions [37–47]. However, fluorine substitution of organic compounds simultaneously elevates their reduction potentials, i.e. organo-fluorine compounds are electrochemically reduced at the higher potentials than those for EC, PC, DMC and DEC [41,42,48,49]. It is therefore important to check charge/discharge behavior of graphite in low potential region in organo-fluorine compound-mixed electrolyte solutions. Among the examined fluorine compounds, many fluoro-carbonates and fluoro-ethers facilitate the formation of solid electrolyte interphase (SEI) on graphite electrode [41–44]. Additionally LiPF_6 contributes to the safety of lithium ion battery. LiF formed by the reaction of LiC_6 with PF_6^- deposits on graphite anode to facilitate SEI formation. LiPF_6 dissociates into LiF and PF_5 at around 100 °C, and LiF may deposit on graphite electrodes. Deposition of LiF on graphite would improve the safety of lithium ion battery because exothermic reactions of LiC_6 with SEI and organic solvents are highly suppressed in LiPF_6 -containing electrolyte solutions, compared with LiClO_4 -containing ones [44]. Deposition of both LiF and decomposed products of organo-fluorine compounds on graphite increases coulombic efficiency at 1st cycle [44]. In the present study, the effect of organo-fluorine compounds on the thermal and oxidation stability of electrolyte solutions and charge/discharge behavior of natural graphite electrode have been investigated to develop new nonflammable solvents for lithium ion batteries.

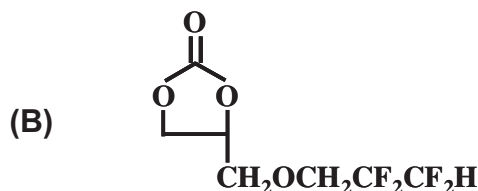
2. Experimental

2.1. Organo-fluorine compounds

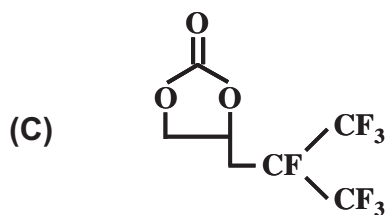
The following organo-fluorine compounds (purity: 99.9%, H_2O : <10 ppm), synthesized in Daikin Industries, Ltd., were used in the present study.



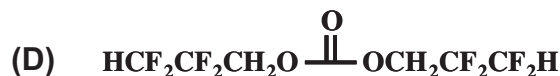
2,2,3,3,3-pentafluoropropyl methanesulfonate



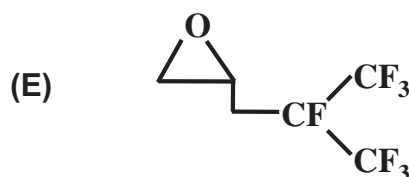
4-[(2,2,3,3,3-tetrafluoropropoxy)methyl]-[1,3]-dioxolan-2-one



4-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl]-[1,3]-dioxolan-2-one



Bis(2,2,3,3,3-tetrafluoropropyl) carbonate



2-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl]-1-oxirane.

Viscosities and specific conductivities of fluorine compounds, **B** and **D** are 4.79 and 0.80 cP at 20 °C, and 5.5×10^{-3} and $8.9 \times 10^{-4} \text{ Scm}^{-1}$ at room temperature, respectively.

2.2. Thermal stability by differential scanning calorimetry (DSC)

Thermal stability of organo-fluorine compound-mixed electrolyte solutions was investigated by DSC (DSC-60, Shimadzu). DSC measurement was carried out using a mixture of electrolyte solution with or without fluorine compound and lithiated or delithiated graphite (NG15 μm) between room temperature and 300 °C at a temperature increasing rate of 5 °C min^{-1} . DSC measurements of only lithiated graphite without electrolyte solution, and reaction of metallic Li with EC/DMC (1:1 vol.) or fluorine compound **A**, **B**, **C** or **E** were also performed in the same manner. Fluorine compound-mixed electrolyte solutions used were 1 mol L^{-1} LiPF_6 -EC/DMC/(**A**, **B**, **C** or **E**) (1:1:1 vol.) and 0.67 mol L^{-1} LiPF_6 -EC/DEC/(**A**, **B**, **C** or **D**) (1:1:1 vol.). The 1 mol L^{-1} LiPF_6 -EC/DMC/(**A**, **B**, **C** or **E**) was prepared by dissolving LiPF_6 into fluorine compound-mixed electrolyte solution. For EC/DEC mixture, 0.67 mol L^{-1} LiPF_6 solutions were used because it is difficult to prepare 1 mol L^{-1} LiPF_6 -EC/DEC/**D** (1:1:1 vol.). Fully lithiated and delithiated graphite samples were electrochemically prepared by 2.5 and 3 cycles corresponding to Li-intercalated and -deintercalated states, respectively. Composition of Li-intercalated graphite samples was calculated from discharge capacity to be $\text{Li}_{0.88-0.98}\text{C}_6$. Lithiated and delithiated graphite samples used for DSC measurements were 1.4–1.6 mg. Electrolyte solution and metallic Li were 3 μL and 9.0–11.0 mg, respectively. To discuss about the reactivity of fluorine compounds with Li, C–O bond lengths were calculated by semi-empirical AM1 method using Spartan '06.

2.3. Electrochemical oxidation current measurements

Oxidation currents were measured by linear sweep of potential at 0.1 mV s^{-1} between 4 and 10 V vs Li/Li^+ for 1 mol L^{-1} LiPF_6 -EC/

DMC (1:1 vol.) and 1 mol L⁻¹ LiPF₆-EC/DMC/(**A**, **B** or **C**) (1:1:1 vol.), and for 1 mol L⁻¹ LiPF₆-EC/DEC (1:1 vol.) and 0.67 mol L⁻¹ LiPF₆-EC/DEC/(**A**, **B**, **C** or **D**) (1:1:1 vol.) by using glassy carbon electrode (diameter: 2.93 mm, geometrical surface area: 1.73 cm²) (Hokuto Denko, HZ-5000). The 1 mol L⁻¹ LiPF₆-EC/DMC/(**A**, **B** or **C**) was prepared by dissolving LiPF₆ into fluorine compound-mixed electrolyte solution. Counter and reference electrodes were Li foil.

2.4. Charge/discharge behavior for NG15 μ m electrode in organo-fluorine compound-mixed electrolyte solutions

Natural graphite powder (purity: >99.95%) with average particle size of 15 μ m (NG15 μ m) was used as an electrode material. The d_{002} value obtained by X-ray diffractometry (XRD-6100, Shimadzu) was 0.3355 nm. Surface area and meso-pore volume obtained by BET surface area measurement (Tristar 3000, Shimadzu) were 6.9 m² g⁻¹ and 0.026 cm³ g⁻¹. D-band to G-band intensity ($R = I_D/I_G$) obtained by Raman spectroscopy (NRS-1000, Jasco) with Nd:YVO₄ laser (532 nm) was 0.25.

Three-electrode cell with natural graphite as a working electrode and Li foil as counter and reference electrodes was used for galvanostatic charge/discharge experiments. Natural graphite electrode was prepared as follows. Natural graphite powder was dispersed in N-methyl-2-pyrrolidone (NMP) containing 12 wt% poly(vinylidene fluoride) (PVdF) and the slurry was pasted on a copper current collector. The electrode was dried at 120 °C under vacuum for half a day. After drying, the electrode contained 80 wt% graphite and 20 wt% PVdF. Electrolyte solutions were prepared by mixing fluorine compound with 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.), 1 mol L⁻¹ LiPF₆-EC/DEC (1:1 vol.) and 1 mol L⁻¹ LiPF₆-EC/EMC/PC (1:1:1 vol.). The 1 mol L⁻¹ LiPF₆-EC/DMC/(**A**, **B**, **C** or **E**) (1:1:1 vol.) and 1 mol L⁻¹ LiPF₆-EC/EMC/PC/(**A**, **B** or **C**) (1:1:1:0.33 or 1:1:1:1.5 vol.) were prepared by dissolving LiPF₆ into fluorine compound-mixed electrolyte solutions. Galvanostatic charge/discharge cyclings were performed using NG15 μ m at a current density of 60 mA g⁻¹ between 0 and 3 V relative to Li/Li⁺ reference electrode at 25 °C (Hokuto Denko, HJ1001 SM8A).

3. Results and discussion

3.1. DSC study on organo-fluorine compound-mixed electrolyte solutions

The reactions of metallic Li with organo-fluorine compounds are shown in Fig. 1. No exothermic reactions were observed below the melting point of Li, 180 °C probably because surface of Li is protected by oxide film. EC/DMC mixture readily reacted with Li just after the melting point of Li. It was already reported that EC and DMC react with Li, yielding lithium alkyl carbonates and lithium

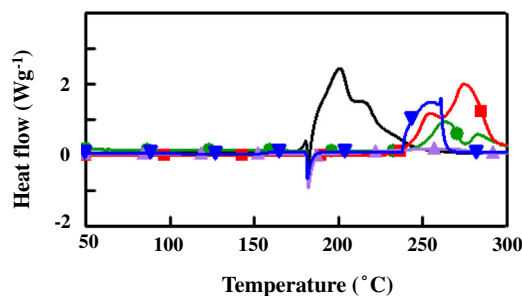


Fig. 1. DSC curves for mixtures of metallic Li and organic solvent or organo-fluorine compound. — EC/DMC(1:1 vol.), — A, — B, — C, — E.

alkoxides [50–52]. However, exothermic reactions started at 238 °C for fluorine compounds, **B**, **C** and **E**, and their exothermic peaks were found between 250 and 300 °C. This result is similar to that obtained for fluoro-ethers and fluoro-carbonate, reported in a previous paper [44]. It is interesting that fluorine-containing methanesulfonate, **A** is very stable, showing no exothermic peak up to 300 °C, which means that **A** neither reacts with Li nor thermally decomposes below 300 °C. Fluorine compounds, **B**, **C** and **E** also have much better thermal stability than EC/DMC mixture.

Fig. 2 shows DSC data obtained when 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.) and 1 mol L⁻¹ LiPF₆-EC/DMC/(**A**, **B**, **C** or **E**) (1:1:1 vol.) were used. Mixtures of delithiated graphite and electrolyte solution with or without fluorine compound gave weak exothermic peaks at around 100 °C and strong ones between 258 and 268 °C (Fig. 2a). The weak peaks at around 100 °C are attributed to the reactions of electrolyte solution with PF₅ generated by the dissociation of LiPF₆, and strong ones at 258–268 °C are mainly due to thermal decomposition of electrolyte solutions [53–57]. Exothermic heats are smaller in fluorine compound-mixed solutions than 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.). Fig. 2b exhibits DSC curves of only lithiated graphite samples prepared in 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.) and 1 mol L⁻¹ LiPF₆-EC/DMC/(**A**, **B** or **C**) (1:1:1 vol.). LiC₆ prepared in 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.) yielded a weak peak at 140 °C

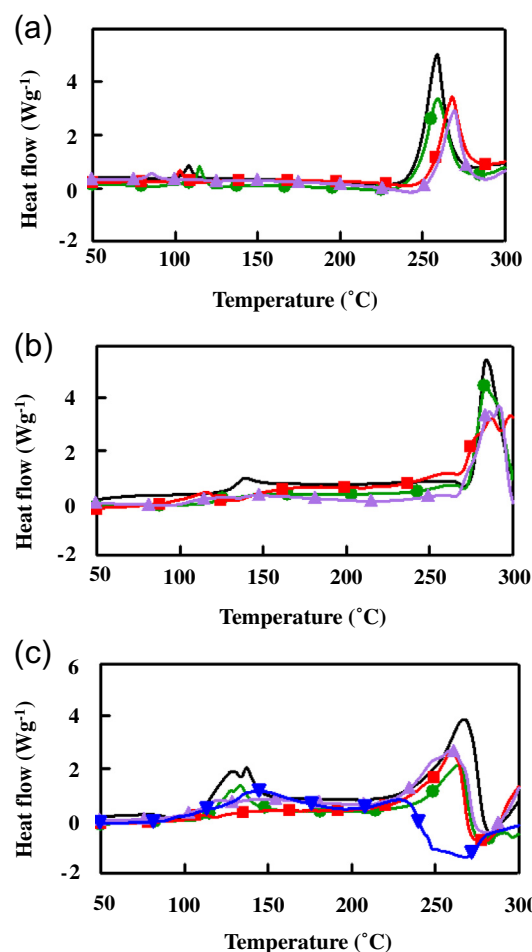


Fig. 2. DSC curves for mixtures of 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.) or 1 mol L⁻¹-LiPF₆ EC/DMC/(**A**, **B** or **C**) (1:1:1 vol.) and delithiated graphite with SEI film (a), only lithiated graphite samples (Li_{0.90-0.98}C₆) with SEI film (b), and mixtures of 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.) or 1 mol L⁻¹ LiPF₆-EC/DMC/(**A**, **B**, **C** or **E**) (1:1:1 vol.) and lithiated graphite (Li_{0.90-0.98}C₆) with SEI film (c). — EC/DMC, — EC/DMC/**A**, — EC/DMC/**B**, — EC/DMC/**C**, — EC/DMC/**E**.

and a strong one at 283 °C. The former is caused by the reaction of Li released from graphite with SEI, and the latter is due to thermal decomposition of SEI [53–57]. However, the $\text{Li}_{0.90-0.98}\text{C}_6$ samples prepared in 1 mol L⁻¹ LiPF₆-EC/DMC/(A, B or C) (1:1:1 vol.) gave no peaks at around 140 °C and the exothermic peaks due to decomposition of SEI are somewhat weaker as shown in Fig. 2b. This may be ascribed to the higher stability of fluorine compound-derived SEIs containing CF₂ and CF₃ groups. Fig. 2c shows DSC profiles for mixtures of lithiated graphite and 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.) or 1 mol L⁻¹ LiPF₆-EC/DMC/(A, B, C or E) (1:1:1 vol.). It was found that mixing of fluorine compounds, A, B and E by 10 vol% was not enough. The observed DSC profiles for mixtures of lithiated graphite and 1 mol L⁻¹ LiPF₆-EC/DMC/(A, B or E) (1:1:0.2 vol.) were similar to that for a mixture of 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.) and lithiated graphite. The effect of mixing of fluorine compounds was found when they were mixed by 33 vol% as shown in Fig. 2c. The exothermic peaks between 100 and 150 °C due to the reactions with $\text{Li}_{0.90-0.98}\text{C}_6$ and those between 230 and 300 °C by the thermal decomposition of electrolyte solutions and SEIs are both weakened in the cases of fluorine compound-mixed electrolyte solutions. Endothermic peaks are mixed between 240 and 300 °C in Fig. 2c, which is attributed to the exfoliation of graphite by final decomposition of Li-intercalated graphite [52]. Among four fluorine compounds, A, B, C and E, exothermic peak was the weakest in E-mixed solution (Fig. 2c). Similar results were obtained for 1 mol L⁻¹ LiPF₆-EC/DEC (1:1 vol.) and 0.67 mol L⁻¹ LiPF₆-EC/DEC/(A, B, C or D) (1:1:1 vol.) as shown in Fig. 3. Exothermic peaks caused by the reactions of PF₅ with organic solvents are weakened and those due to thermal decomposition of electrolyte solutions are reduced and shifted to higher temperatures (Fig. 3a). Intensity of exothermic peaks was weakened for the reactions of $\text{Li}_{0.88-0.96}\text{C}_6$ with SEI and organic solvents between 100 and 150 °C, and also for thermal decomposition of electrolyte solutions and SEI between 235 and 300 °C (Fig. 3b). In D-mixed solution, the exothermic peak between

100 and 150 °C had a similar profile to that obtained in 1 mol L⁻¹ LiPF₆-EC/DEC (1:1 vol.) and another peak observed at high temperature was shifted to 290 °C. The results of DSC measurements indicate that the reactivity with LiC₆ between 100 and 150 °C and thermal decomposition of electrolyte solution and SEI between 235 and 300 °C are both suppressed by mixing of fluorine compounds.

3.2. Oxidation current measurements in organo-fluorine compound-mixed electrolyte solutions

Electrochemical oxidation stability of electrolyte solutions was examined by oxidation current measurements using glassy carbon electrode. Fig. 4 shows the oxidation currents measured in electrolyte solutions with or without fluorine compound. Oxidation currents had current peaks as shown in Fig. 4a₁ and b₁, and no current was observed after the peaks. This phenomenon would be a so-called “anode effect” usually observed in the electrolytic production of F₂ gas using a carbon anode. Once anode effect happens, anode potential highly increases and simultaneously current falls down to zero. Glassy carbon would be fluorinated by oxidative decomposition of PF₆⁻ anion at a high potential, yielding hydrophobic carbon-fluorine (CF) film. The wettability of electrolyte with glassy carbon is extremely reduced by the formation of hydrophobic CF film, which leads to the occurrence of anode effect. Oxidation current peaks were situated at the higher potentials in fluorine compound-mixed electrolyte solutions than in original 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.) and -EC/DEC (1:1 vol.). As shown in Fig. 4a₂ and b₂, oxidation currents started to increase at 6.5 V and 6.7 V relative to Li/Li⁺ in 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.) and -EC/DEC (1:1 vol.), respectively. Overpotential of carbon anode is usually large in fluoride solution due to the formation of CF film. Oxidation currents were clearly reduced in both 1 mol L⁻¹ LiPF₆-EC/DMC/(A, B or C) (1:1:1 vol.) and 0.67 mol L⁻¹ LiPF₆-EC/DEC/(A, B, C or D) (1:1:1 vol.), compared with those in original solutions without fluorine compounds. This would be due to the high stability of fluorine compounds against electrochemical oxidation. The reduction in the oxidation currents would be due to decrease in the electrode surface area of glassy carbon by adsorption of stable fluorine compounds. Among four fluorine compounds, A, B and C gave slightly better results than D.

3.3. Charge/discharge behavior for natural graphite electrode in organo-fluorine compound-mixed electrolyte solutions

Charge/discharge characteristics of natural graphite electrode was investigated in several electrolyte solutions containing fluorine compounds. Fig. 5 shows charge/discharge potential curves at 1st cycle in 1 mol L⁻¹ LiPF₆-EC/DMC (1:1:1 vol.) and 1 mol L⁻¹ LiPF₆-EC/DMC/(A, B, C or E) (1:1:1 vol.) at 60 mA g⁻¹. Electrode potentials quickly decreased except that in 1 mol L⁻¹ LiPF₆-EC/DMC/E (1:1:1 vol.), in which short potential plateau indicating the reduction of E was observed. In 1 mol L⁻¹ LiPF₆-EC/DEC (1:1:1 vol.) and 0.67 mol L⁻¹ LiPF₆-EC/DEC/(A, B, C or D) (1:1:1 vol.), all discharge potential curves were nearly the same without potential plateau corresponding to the reduction of fluorine compounds (Fig. 6). Tables 1 and 2 summarize charge/discharge capacities and first coulombic efficiencies obtained in these EC-based solvents. First coulombic efficiencies obtained in fluorine compound-mixed electrolyte solutions were similar to those obtained in 1 mol L⁻¹ LiPF₆-EC/DMC (1:1:1 vol.) and -EC/DEC (1:1:1 vol.) without fluorine compounds except first coulombic efficiency in 1 mol L⁻¹ LiPF₆-EC/DMC/E (1:1:1 vol.). Contribution of E to SEI formation is slightly lower than others. Charge capacities in 1 mol L⁻¹ LiPF₆-EC/DMC/(A, B, C or E) (1:1:1 vol.) and 0.67 mol L⁻¹ LiPF₆-EC/DEC/(B or C) (1:1:1 vol.) were slightly lower than those in the original electrolyte

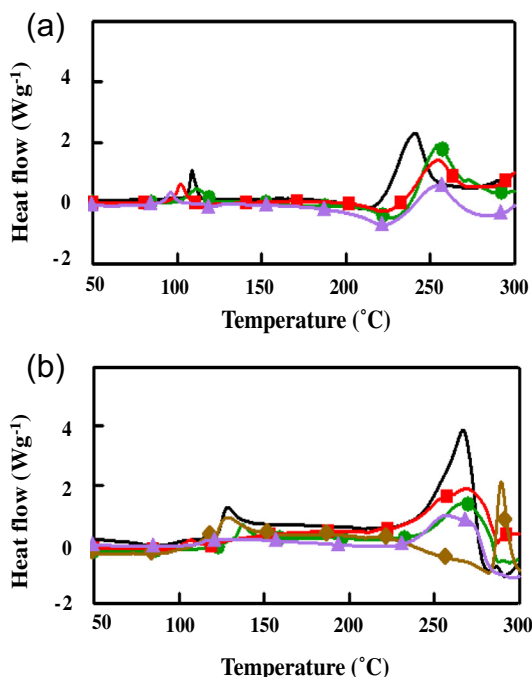


Fig. 3. DSC curves for mixtures of 1 mol L⁻¹ LiPF₆-EC/DEC (1:1 vol.) or 0.67 mol L⁻¹ LiPF₆-EC/DEC/(A, B or C) (1:1:1 vol.) and delithiated graphite with SEI film (a), and mixtures of 1 mol L⁻¹ LiPF₆-EC/DEC (1:1 vol.) or 0.67 mol L⁻¹ LiPF₆-EC/DEC/(A, B, C or D) (1:1:1 vol.) and lithiated graphite ($\text{Li}_{0.88-0.96}\text{C}_6$) with SEI film (b). — EC/DEC, —△— EC/DEC/A, —●— EC/DEC/B, —■— EC/DEC/C, —◆— EC/DEC/D.

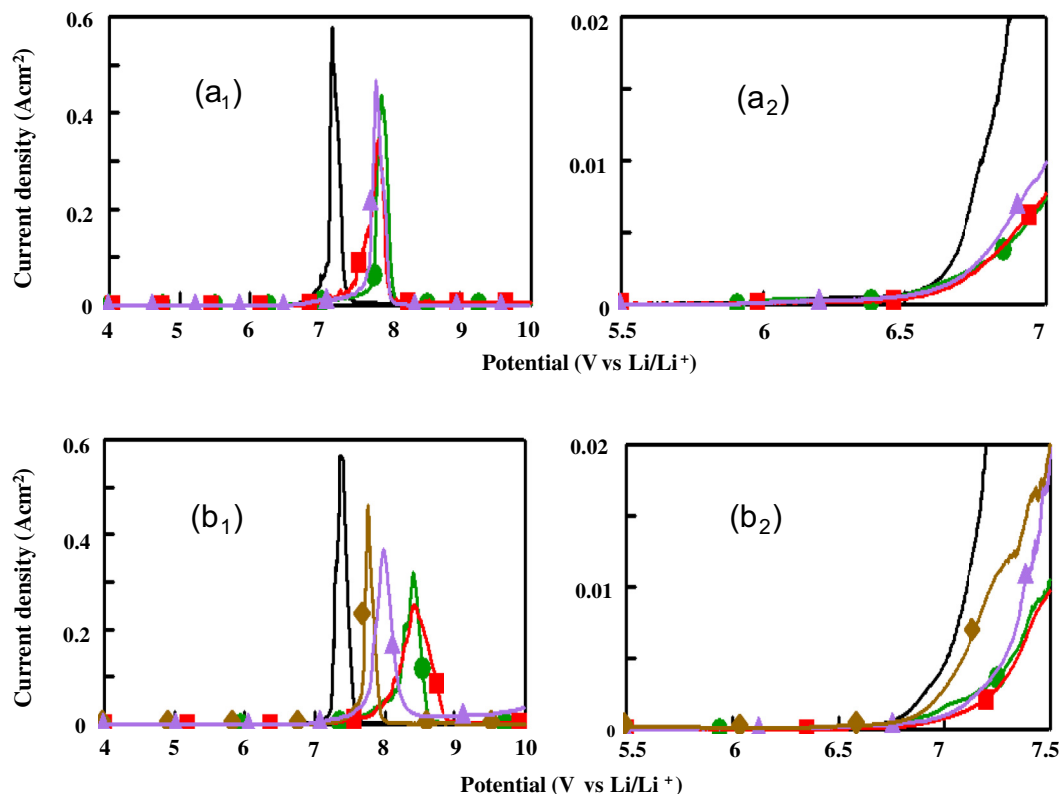


Fig. 4. Linear sweep voltammograms for glassy carbon electrode in 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.) and 1 mol L⁻¹ LiPF₆-EC/DMC/(A, B or C) (1:1:1 vol.) (a₁ and a₂), and in 1 mol L⁻¹ LiPF₆-EC/DEC (1:1 vol.) and 0.67 mol L⁻¹ LiPF₆-EC/DEC/(A, B, C or D) (1:1:1 vol.) (b₁ and b₂). — EC/DMC and EC/DEC, —▲— EC/DMC/A and EC/DEC/A, —●— EC/DMC/B and EC/DEC/B, —■— EC/DMC/C and EC/DEC/C, —◆— EC/DMC/D.

solutions without fluorine compound (Tables 1 and 2). This is probably because SEI resistances were slightly increased by the deposition of fluorides. The obtained results indicate that fluorine compounds, **A**, **B** and **C** can be used for 1 mol L⁻¹ LiPF₆-EC/DMC (1:1:1 vol.) and -EC/DEC (1:1:1 vol.). Unfortunately it is difficult to prepare 1 mol L⁻¹ LiPF₆-EC/DEC/**D** (1:1:1 vol.) because solubility of LiPF₆ is not enough as mentioned in the experimental section, 2.2. The effect of mixing of fluorine compounds was also examined using PC-containing electrolyte solutions. Fig. 7 shows charge/discharge potential curves at 1st cycle in 1 mol L⁻¹ LiPF₆-EC/EMC/PC/(A, B or C) (1:1:1:0.33 or 1:1:1:1.5 vol.). The potential plateau observed in 1 mol L⁻¹ LiPF₆-EC/EMC/PC (1:1:1 vol.) indicates electrochemical reduction of PC. However, the potential plateau

almost disappeared in fluorine compound-mixed solutions. Table 3 gives electrochemical data obtained in PC-containing solutions. First coulombic efficiencies were largely increased by mixing of fluorine compounds without decrease in capacities. First coulombic efficiencies were in the range of 69–74% when **A**, **B** and **C** were mixed by 10 vol%, but it reached 81% when **A** was mixed by 33 vol%. The increments of first coulombic efficiencies were in the range of 16–20% in 1 mol L⁻¹ LiPF₆-EC/EMC/PC/(A, B or C) (1:1:1:0.33 vol.), and 28% in 1 mol L⁻¹ LiPF₆-EC/EMC/PC/A (1:1:1:1.5 vol.) at 60 mA g⁻¹. This means that fluorine compounds, **A**, **B** and **C** effectively facilitate SEI formation in PC-containing electrolyte solution. Fluorine compounds, **A**, **B**, **C** and **D** gave the better results than **E** in the charge/discharge experiments.

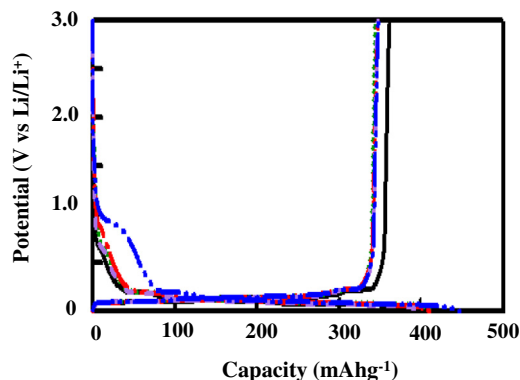


Fig. 5. First charge/discharge curves of NG15 μ m electrode in 1 mol L⁻¹ LiPF₆-EC/DMC (1:1:1 vol.) and 1 mol L⁻¹ LiPF₆-EC/DMC/(A, B, C or E) (1:1:1 vol.) at 60 mA g⁻¹. — EC/DMC, - - - EC/DMC/A, EC/DMC/B, - · - · - EC/DMC/C, - - - EC/DMC/E.

3.4. Influence of molecular structures of fluorine compounds on the thermal stability and electrochemical properties

Electrochemical oxidation stability, reactivity with Li and charge/discharge characteristics have been investigated using organo-fluorine compounds such as cyclic and linear fluoro-carbonates, linear and cyclic fluoro-ethers and fluoro-sulfonate in the present and previous studies [41–44].

Oxidation current measurements in fluorine compound-mixed electrolyte solutions were made using Pt electrode for LiClO₄-containing solutions [41–44] or glassy carbon electrode for LiPF₆-containing ones [44]. Fluoro-sulfonate, **A**, cyclic fluoro-carbonates, **B** and **C**, and linear fluoro-ethers, CHF₂CF₂CH₂OCF₂CHF₂ and CHF₂CF₂CH₂OCF₂CHFCI [44] show high oxidation stability. Oxidation currents measured in the electrolyte solutions containing linear fluoro-carbonates, **D**, CF₃CH₂OCO₂CH₃ and CF₃CH₂O-CO₂CH₂CF₃ [42,43] were slightly larger than those for the cyclic

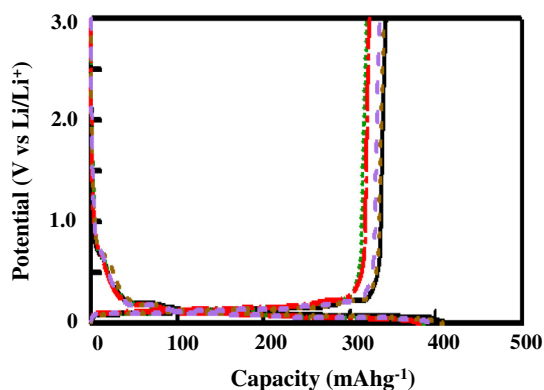


Fig. 6. First charge/discharge curves of NG15 μm electrode in 1 mol L^{-1} $\text{LiPF}_6\text{-EC/DEC}$ (1:1 vol.) and 0.67 mol L^{-1} $\text{LiPF}_6\text{-EC/DEC/(A, B, C or D)}$ (1:1:1 vol.) at 60 mA g^{-1} . — EC/DEC, — EC/DEC/A, — EC/DEC/B, — EC/DEC/C, — EC/DEC/D.

fluoro-carbonates and linear fluoro-ethers mentioned above though they were smaller than those obtained in the original solutions without fluorine compounds.

Reactivity of fluorine compounds with metallic Li and Li_6C are low. Fluoro-sulfonate, A and linear fluoro-ethers, $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CHF}_2$ and $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CHFCl}$ [44] are very stable against metallic Li. Fluoro-sulfonate, A does not react with metallic Li up to 300 °C. The linear fluoro-ethers give exothermic peaks between 250 and 300 °C close to the thermal decomposition temperature [44]. Cyclic carbonates, B and C, another cyclic carbonate similar to B [44], and cyclic ether, E are also stable, starting to react with metallic Li at somewhat lower temperatures of 226–238 °C. The electrolyte solutions containing fluoro-sulfonate, cyclic and linear fluoro-carbonates, and linear and cyclic fluoro-ethers by 33 vol% show good stability against Li_6C [43,44].

Electrochemical reduction of fluorine compounds is initiated at the higher potentials (1.9–2.7 V vs Li/Li^+) [41,42] than those of EC, PC, DEC and DMC (1.3–1.6 V) [48,49]. If decomposed products are insoluble or their solubilities are very low in the electrolyte solutions, they can contribute to the formation of SEI. It is enough for the contribution to SEI formation if small amounts of insoluble or low solubility products are formed by electrochemical reduction of fluorine compounds. Fluorine compounds having long ligands consisting of C, H and F may yield low solubility products. Fluoro-sulfonate, A, fluoro-carbonates, B, C and D, and fluoro-ether, $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CHF}_2$ [44] give high first coulombic efficiencies without increase in irreversible capacities in EC-based electrolyte solutions. Fluoro-sulfonate, A, cyclic fluoro-carbonates, B and C, linear fluoro-carbonates, D, $\text{CF}_3\text{CH}_2\text{OCO}_2\text{CH}_3$ and $\text{CF}_3\text{CH}_2\text{O-CO}_2\text{CH}_2\text{CF}_3$ [42,43], and linear fluoro-ethers, $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CHF}_2$

Table 1
Charge/discharge capacities and coulombic efficiencies of NG15 μm in 1 mol L^{-1} $\text{LiPF}_6\text{-EC/DMC}$ (1:1 vol.) and 1 mol L^{-1} $\text{LiPF}_6\text{-EC/DMC/(A, B, C or E)}$ (1:1:1 vol.) at 60 mA g^{-1} .

Electrolyte solution	Cycle number	Discharge capacity (mAhg^{-1})	Charge capacity (mAhg^{-1})	Coulombic efficiency (%)
EC/DMC	1st	413	361	87.6
	10th	360	358	99.5
EC/DMC/A	1st	404	347	85.8
	10th	340	339	99.6
EC/DMC/B	1st	415	344	83.0
	10th	335	333	99.4
EC/DMC/C	1st	411	347	84.5
	10th	315	314	99.5
EC/DMC/E	1st	447	348	77.8
	10th	341	337	98.8

Table 2

Charge/discharge capacities and coulombic efficiencies of NG15 μm in 1 mol L^{-1} $\text{LiPF}_6\text{-EC/DEC}$ (1:1 vol.) and 0.67 mol L^{-1} $\text{LiPF}_6\text{-EC/DEC/(A, B, C or D)}$ (1:1:1 vol.) at 60 mA g^{-1} .

Electrolyte solution	Cycle number	Discharge capacity (mAh g^{-1})	Charge capacity (mAh g^{-1})	Coulombic efficiency (%)
EC/DEC	1st	412	342	83.0
	10th	338	336	99.5
EC/DEC/A	1st	400	334	83.6
	10th	332	330	99.4
EC/DEC/B	1st	387	320	82.7
	10th	321	319	99.3
EC/DEC/C	1st	391	322	82.0
	10th	284	282	99.2
EC/DEC/D	1st	409	340	83.1
	10th	339	335	99.1

and $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CHFCl}$ [44] increase first coulombic efficiencies in PC-mixed solutions. Thus most of the fluorine compounds hitherto examined contribute to the SEI formation. In particular, fluoro-sulfonate, A, cyclic fluoro-carbonate, C, and linear fluoro-ether, $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CHF}_2$ [44] give high first coulombic efficiencies in PC-mixed solutions.

Fluorine substitution decreases HOMO and LUMO levels of organic compounds [41,42]. It means that organo-fluorine compounds used in the present and previous studies are stable against oxidation, but easily reduced. This is due to the strong electron-withdrawing ability of fluorine atom. The decrease in HOMO levels by fluorine substitution of organic compounds makes difficult electron extraction from fluorine compounds (oxidation

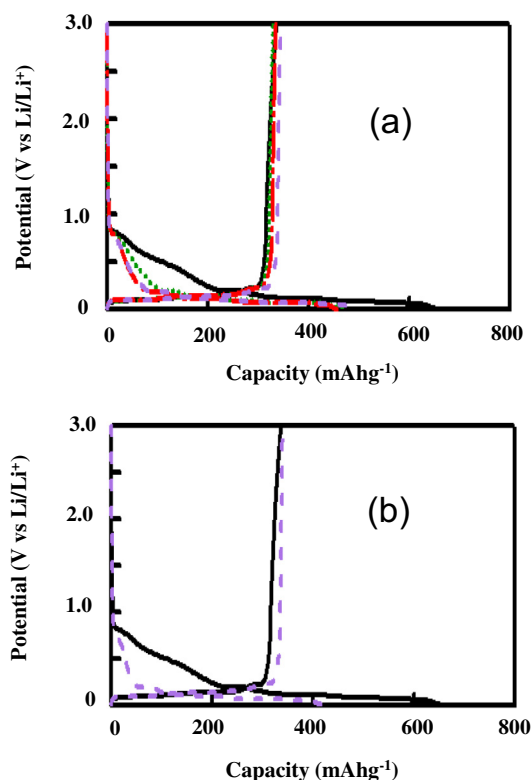


Fig. 7. First charge/discharge curves of NG15 μm electrode at 60 mA g^{-1} in 1 mol L^{-1} $\text{LiPF}_6\text{-EC/EMC/PC}$ (1:1:1 vol.) and 1 mol L^{-1} $\text{LiPF}_6\text{-EC/EMC/PC/(A, B or C)}$ (1:1:1:0.33 vol.) (a), and in 1 mol L^{-1} $\text{LiPF}_6\text{-EC/EMC/PC}$ (1:1:1 vol.) and 1 mol L^{-1} $\text{LiPF}_6\text{-EC/EMC/PC/A}$ (1:1:1:1.5 vol.) (b). — EC/EMC/PC, — EC/EMC/PC/A, — EC/EMC/PC/B, — EC/EMC/PC/C.

Table 3

Charge/discharge capacities and coulombic efficiencies of NG15 μm in 1 mol L⁻¹ LiPF₆-EC/EMC/PC (1:1:1 vol.), 1 mol L⁻¹ LiPF₆-EC/EMC/PC/(**A**, **B** or **C**) (1:1:1:0.33 vol.) and 1 mol L⁻¹ LiPF₆-EC/EMC/PC/**A** (1:1:1:1.5 vol.) at 60 mA g⁻¹.

Electrolyte solution	Cycle number	Discharge capacity (mAhg ⁻¹)	Charge capacity (mAhg ⁻¹)	Coulombic efficiency (%)
EC/EMC/PC (1:1:1:0.33)	1st	630	337	53.5
	10th	337	333	98.6
EC/EMC/PC/ A (1:1:1:0.33)	1st	486	342	70.3
	10th	335	331	98.8
EC/EMC/PC/ B (1:1:1:0.33)	1st	476	326	69.3
	10th	315	311	98.7
EC/EMC/PC/ C (1:1:1:0.33)	1st	456	335	73.5
	10th	313	309	98.7
EC/EMC/PC/ A (1:1:1:1.5)	1st	419	340	81.2
	10th	327	324	99.2

reaction). Reaction with Li and electrochemical reduction are both reductive reactions. Nevertheless the fluorine substitution reduces the reactivity of fluorine compounds with metallic Li and LiC₆. It seems that the low reactivity of fluorine compounds with metallic Li and LiC₆ is due to difficulty in the formation of Li salts or slow reaction rates for the formation of Li salts. Linear fluoro-carbonates are composed of $-\text{CH}_2-\text{O}-\text{CF}_2-$ in which O is bonded with CH₂ and CF₂. The C–O bond lengths of $-\text{O}-\text{CH}_2\text{CF}_2\text{CHF}_2$ and $-\text{O}-\text{CF}_2\text{CHF}_2$ in $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CHF}_2$ are 1.425 and 1.407 nm, respectively. Therefore the direct contact of Li atom with O of $-\text{CH}_2-\text{O}-\text{CF}_2-$ is not easy, i.e. reactivity of the linear fluoro-carbonates with Li is low. Reduction currents for linear fluoro-ethers are also small as reported in a previous paper [42]. In cyclic fluoro-carbonates, **B** and **C**, the C–O bond lengths of $-\text{O}-\text{CH}(\text{CH}_2\text{R}_f)-$ (R_f: ligand composed of C, H, F and O) and $-\text{O}-\text{CH}_2-$ are longer than those of $\text{O}=\text{C}(-\text{O})_2-$ ($-\text{O}-\text{CH}(\text{CH}_2\text{R}_f)-$: 1.446 nm; $-\text{O}-\text{CH}_2-$: 1.441–1.442 nm; $\text{O}=\text{C}(-\text{O})_2-$: 1.368–1.373 nm). This suggests that the C–O bonds of $-\text{O}-\text{CH}(\text{CH}_2\text{R}_f)-$ is broken by the reaction with Li. However, formation of Li salts may not proceed smoothly because of the long R_f ligands of **B** and **C**. In the case of linear fluoro-carbonates, **D**, $\text{CF}_3\text{CH}_2\text{O}-\text{CO}_2\text{CH}_3$ and $\text{CF}_3\text{CH}_2\text{OCO}_2\text{CH}_2\text{CF}_3$, Li salts such as $\text{CHF}_2\text{CH}_2\text{OCO}_2\text{Li}$, $\text{CF}_3\text{CH}_2\text{OCO}_2\text{Li}$ and $\text{CF}_3\text{CH}_2\text{OCO}_2\text{Li}$, respectively, may be more easily formed than those of cyclic fluoro-carbonates having long R_f ligands. The C–O bonds of $-\text{O}-\text{CH}_2\text{CF}_2\text{CHF}_2$, $-\text{O}-\text{CH}_2\text{CF}_3$ and $-\text{O}-\text{CH}_3$ may be broken by the reactions with Li because they are longer than those of $\text{O}=\text{C}(-\text{O})_2-$ ($-\text{O}-\text{CH}_2\text{CF}_2\text{CHF}_2$ and $\text{O}=\text{C}(-\text{O})_2-$ of **D**: 1.425–1.428 and 1.352–1.363 nm, respectively; $-\text{O}-\text{CH}_2\text{CF}_3$, $-\text{O}-\text{CH}_3$ and $\text{O}=\text{C}(-\text{O})_2-$ of $\text{CF}_3\text{CH}_2\text{OCO}_2\text{CH}_3$: 1.419–1.423, 1.436–1.438 and 1.344–1.369 nm, respectively; $-\text{O}-\text{CH}_2\text{CF}_3$ and $\text{O}=\text{C}(-\text{O})_2-$ of $\text{CF}_3\text{CH}_2\text{OCO}_2\text{CH}_2\text{CF}_3$: 1.422–1.426 and 1.354–1.364 nm, respectively). The above C–O bond lengths are slightly different depending on cis-trans conformations of ligands composed of C, H and F. The fluorine compounds hitherto investigated are electrochemically reduced at the higher potentials, i.e. more easily reduced than EC, PC, DEC and DMC [41,42,48,49]. This may be due to large decrease in activation energies for electrochemical reduction reaction of fluorine compounds by strong electron-withdrawing fluorine. Cathodic reduction of fluorine compounds accompanying C–O bond breaking may be facilitated by fluorine.

4. Conclusions

Thermal stability and electrochemical oxidation stability of fluorine compound-mixed electrolyte solutions have been investigated by DSC and oxidation current measurement. Charge/discharge behavior of NG15 μm has been also examined using the same electrolyte solutions. Fluorine compound, **A** did not react with metallic Li below 300 °C, and **B**, **C** and **E** had much lower reactivity

with metallic Li than EC/DMC. The 1 mol L⁻¹ LiPF₆-EC/DMC/(**A**, **B**, **C** or **E**) (1:1:1 vol.) and 0.67 mol L⁻¹ LiPF₆-EC/DEC/(**A**, **B** or **C**) (1:1:1 vol.) showed the lower reactivity with LiC₆ between 100 and 150 °C. Exothermic peaks by the decomposition of electrolyte solutions and SEIs were also smaller in 1 mol L⁻¹ LiPF₆-EC/DMC/(**A**, **B**, **C** or **E**) (1:1:1 vol.) and 0.67 mol L⁻¹ LiPF₆-EC/DEC/(**A**, **B**, **C** or **D**) (1:1:1 vol.) than in 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.) and -EC/DEC (1:1 vol.) without fluorine compound, respectively. Oxidation currents measured using glassy carbon were smaller in 1 mol L⁻¹ LiPF₆-EC/DMC/(**A**, **B** or **C**) (1:1:1 vol.) and 0.67 mol L⁻¹ LiPF₆-EC/DEC/(**A**, **B**, **C** or **D**) (1:1:1 vol.) than in 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.) and 1 mol L⁻¹ LiPF₆-EC/DEC (1:1 vol.), respectively. Fluorine compounds, **A**, **B** and **C**-mixed electrolyte solutions gave the smaller oxidation currents than **D**-mixed one. First coulombic efficiencies obtained in 1 mol L⁻¹ LiPF₆-EC/DMC/(**A**, **B**, or **C**) (1:1:1 vol.) and 0.67 mol L⁻¹ LiPF₆-EC/DEC/(**A**, **B**, **C** or **D**) (1:1:1 vol.) were similar to those in original 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 vol.) and -EC/DEC (1:1 vol.). Somewhat lower first coulombic efficiency was obtained in 1 mol L⁻¹ LiPF₆-EC/DMC/**E** (1:1:1 vol.). Mixing of fluorine compound is effective for PC-containing electrolyte solution. First coulombic efficiencies highly increased in 1 mol L⁻¹ LiPF₆-EC/EMC/PC/(**A**, **B** or **C**) (1:1:1:0.33 vol.) and 1 mol L⁻¹ LiPF₆-EC/EMC/PC/**A** (1:1:1:1.5 vol.), compared with that obtained in 1 mol L⁻¹ LiPF₆-EC/EMC/PC (1:1:1 vol.). Considering the results obtained by DSC, oxidation current measurement and charge/discharge cycling, fluorine compounds, **A**, **B** and **C** are better than **D** and **E** as new solvents with high stability for lithium ion battery.

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